

Matrix effects on the stability of toxic hydrocarbons stored in Tedlar bags for vehicle exhaust emissions testing

Michael E. Gebel¹, Luis F. Woodhouse³, Jinyou Liang², Ajith Kaduwela³, Julia G. Sandoval¹, Paul L. Rieger¹, and Mark Fuentes¹

¹California Air Resources Board, Monitoring and Laboratory Division, 9528 Telstar Avenue, El Monte, CA 91731. ²Bay Area Air Quality Management District, Planning Division, 939 Ellis Street, San Francisco, CA 94109.

³California Air Resources Board, Planning and Technical Support Division, 1001 I Street, Sacramento, CA 95814

Introduction

Increasingly, there has been interest in measuring the gas phase emissions of specific toxic hydrocarbon species like BTEX and 1,3-butadiene in exhaust

Because these analyses may not be performed until several hours after the completion of an emissions test, the stability of these species in the exhaust matrix is very important

Previous work has shown that although BTEX and most other hydrocarbon species are stable in gasoline exhaust samples, 1,3-butadiene concentration continually decreases with residence time in the bag. Over 25% in 24 hrs. and 70% in 48 hrs. [Lipari, 1990]

This study examines the stability of toxic species in both gasoline and diesel vehicle exhaust and investigates the loss processes

The implications of such loss processes on the determination of accurate toxic emission factors is discussed

Methodology

Samples of exhaust from 2 light duty trucks and one diesel school bus were obtained from unrelated ARB emissions testing projects and then subjected to a gas phase hydrocarbon speciation analysis method

The concentrations of the specialized compounds in these samples were measured multiple times over a period of up to one day in order to determine if any appreciable loss of specific hydrocarbons occurred

An atmospheric oxidation model was used to determine if any measured losses could be explained by chemistry occurring in the sample bag during the holding period before GC analysis

This model was also used to illustrate the higher potential for 1,3-butadiene decay with time for conditions typical of diesel exhaust matrices

Experimental Method

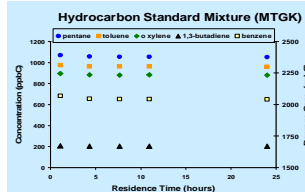
For each of the three vehicles, a small bag of exhaust was taken from only one of the phases of a complete vehicle emissions test cycle (CVS systems)

The concentrations of specific hydrocarbons in the samples were then determined using the analytical method described in the California Non-Methane Organic Test Procedures [Parts D & E]

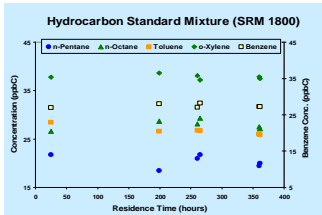
The concentrations of several hydrocarbon species, including BTEX and 1,3-butadiene, were plotted as a function of residence time in the bag before analysis

Hydrocarbon standard mixtures were also analyzed in the same manner in order to confirm their stability in the absence of a reactive exhaust matrix

Stability of Standards in Tedlar Bags



High concentration standard mixtures are stable to within 2% of initial values for over 24 hours in the bag

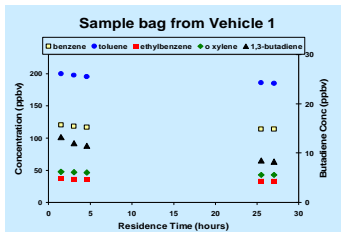


Measurements of low concentration standard mixtures are more variable, but they do not show statistically significant decay (> 2 std. dev.) over a two week period in the bag

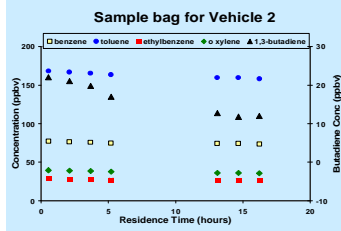
Stability in Gasoline Vehicle Exhaust

Exhaust samples were taken from the cold start portion of an FTP driving cycle shortly after completion of the test then analyzed repeatedly over a period of up to one day

Two vehicles were arbitrarily selected from ongoing surveillance testing programs at ARB; Vehicle 1 was a 1995 light duty truck; Vehicle 2 was a 2000 light duty truck (these vehicles were chosen for their relatively high emissions)



Vehicle 1 shows ~ 40% loss of 1,3-butadiene in one day and < 10% loss of BTEX compounds in over 24 hrs.



Vehicle 2 shows ~ 40% loss of 1,3-butadiene in 16 hrs. and < 7% loss of BTEX compounds in 16 hrs.

What Causes 1,3-Butadiene Loss?

Because 1,3-butadiene standards are stable in Tedlar bags for over 24 hours, so the loss in exhaust samples must be due to reaction with other species present in the matrix

In the air, 1,3-butadiene is removed primarily by reaction with free radicals (OH, O₃, NO₃).

1,3-butadiene can also react with NO₂ but this reaction is typically too slow to be considered in atmospheric oxidation models. However, under conditions of very high [NO_x] like that present in exhaust matrices this reaction can dominate.

Reaction rates of 1,3-butadiene are [Atkinson, 1997]:
with OH $k = 6.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
with O₃ $k = 6.3 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
with NO₂ $k = 1.0 \times 10^{-31} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
with NO₂ $k = 3.0 \times 10^{-30} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

We can estimate the loss of 1,3-butadiene from these processes by using an atmospheric oxidation model with the initial conditions present in the exhaust sample bag (dark simulation)

Model Description

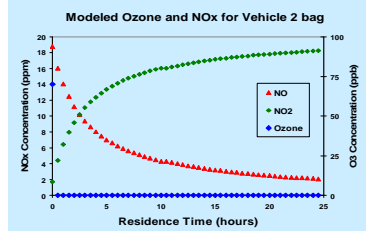
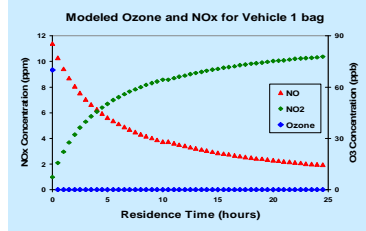
We are using a box-model with the master chemical mechanism (MCM) and the SMVGAEAR solver, an ordinary differential equation solver [Jacobson, 1998]

The current version of the MCM (version 3.0) describes the complete tropospheric oxidation of 124 VOCs. It has 5631 thermal reactions and 1830 photolytic reactions. The oxidation is initiated by reaction with OH and, where appropriate, direct photolysis and the reactions with O₃ and NO₂. It can be downloaded at <http://130.95.40.171>.

The degradation schemes are described by Saunders *et al.* [2002,2003] and Jenkin *et al.* [2002, 2003].

Simulations were run in the dark and additional reactions were added for 1,3-butadiene + NO₂ [rate from Atkinson, 1997], the oxidation of NO by oxygen at high NO [rate from Finlayson-Pitts & Pitts, 2000], and an estimated surface removal of NO_x (forming nitrous and nitric acid in the presence of water)

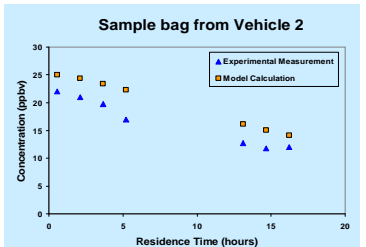
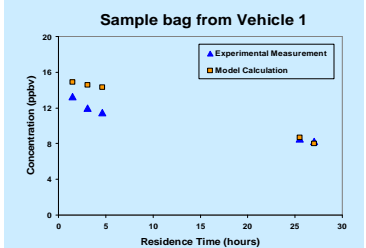
Model Results - Oxidants



Model Results - Decay of 1,3-Butadiene

All of the OH, O₃, and NO₃ present in the exhaust matrix (from the ambient dilution air) is removed within minutes due to the high initial NO concentration (only O₃ is plotted above)

NO reacts with oxygen to form NO₂ (Note that this process is second order in NO: $2 \text{ NO} + \text{O}_2 = 2 \text{ NO}_2$)

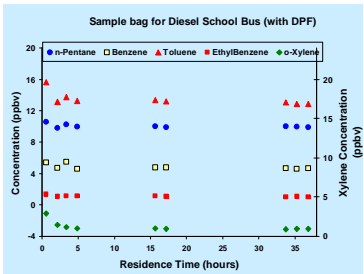


Model in good agreement with measured concentrations suggesting that decay is due to reaction with NO₂

Stability in Diesel Vehicle Exhaust

An exhaust sample was taken from a diesel school bus from the cold start portion of a CBD driving cycle shortly after completion of the test and then analyzed repeatedly over a period of up to one day

This bus was selected from an ongoing testing program at ARB; it was equipped with a diesel particulate filter (DPF)



No 1,3-butadiene was detected in this sample

No hydrocarbon species show continuous decay in the diesel exhaust matrix. Toluene and Xylene show some decay in first few hours of holding time.

Implications for 1,3-butadiene in Diesel

Because 1,3-butadiene shows significant decay in gasoline exhaust samples over time, its actual emission may be under-reported or undetected

This under-reporting is likely to be of greater significance for diesel exhaust samples because they generally have much higher NO_x levels than gasoline samples

Below are some typical conditions for exhaust samples taken from gasoline and diesel vehicles:

Typical Bag Conditions by Fuel Type*

	'90s era gasoline (high emitter)	HD Diesel (transit bus)
Total NMHC	15-150 ppmC	5-20 ppmC
Total NO _x	10-25 ppm	40-60 ppm
NO ₂	~1-5%	~1-5% (20%+ w/DPF)

Note: Sample concentrations are strongly dependent on driving cycle and CVS dilution.

*The above conditions are derived from unpublished ARB data, projects 2S03C1, 2R0302, and 2R0102 based on similar cold start transient driving cycles with similar dilution.

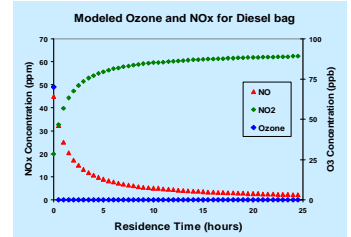
Hypothetical Decay of 1,3-butadiene in Diesel

Due to the fact that no 1,3-butadiene was detected in the diesel sample tested, we must create a hypothetical sample to illustrate the potential decay of 1,3-butadiene in a sample that originally contains a detectable level of the species

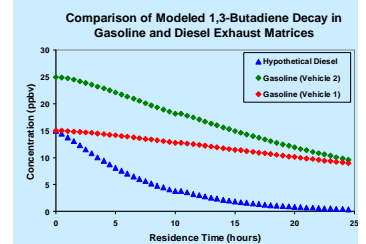
We estimate the loss of 1,3-butadiene in a hypothetical diesel matrix assuming an initial concentration of 15 ppbv and typical NMHC and NO_x levels.

The example below is for a diesel sample from a vehicle with a diesel particulate filter (we have assumed 20% of NO_x is NO₂)

Diesel Model Results - Oxidants



Comparison of Modeled Decay Rates for 1,3-Butadiene



Assuming an initial [1,3-butadiene] of 15 ppbv in diesel exhaust, over 50% is lost in 5 hrs. due to reaction with NO₂.

Conclusions

Hydrocarbon decay mechanisms for exhaust samples can be identified using an atmospheric oxidation model with the appropriate initial conditions

The significant loss of 1,3-butadiene over time in gasoline vehicle exhaust can be attributed to its reaction with NO₂

It is likely that 1,3-butadiene is under-reported in emissions testing and this under-reporting will increase as a function of sample holding time and NO_x concentration

Short lived decay of toluene and xylenes in diesel sample bag is not predicted by the model and may be the result of HC standard carry-over, loss to the wall of the sample bag, or reactions not included in the model that may be important (further investigation is needed)

References

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Note: Data for comparison of both types of exhaust matrices represent a range of unconfirmed raw sample concentration data from projects 2S03C1, 2R0302, and 2R0102. This data should not be used to make any comparisons between the emissions of the two vehicle types.